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## The Molecular Designing of Materials

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**The Molecular Designing of Materials**

by

**A. von Hippel**

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Cambridge, Massachusetts**

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**January, 1962**

# THE MOLECULAR DESIGNING OF MATERIALS\*

by

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Cambridge, Massachusetts

The Web of Electron Clouds - Atom Structure - Elements and Compounds -  
Molecules and Crystals - Laws of Molecular Architecture -  
Structure and Properties

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Exploration of the resources of our planet, only a generation ago still left to the individual prospector, geologist, or mining engineer, is now a joint concern of the scientific world community, as the recent International Geophysical Year testifies. Our present knowledge of mineral resources has just been summarized with penetrating understanding by Dr. Meyerhoff. How to sustain an explosively growing world population is the theme of pioneering studies like those of Prof. Harrison Brown, who was to be chairman of our session. Catastrophe will be the assured outcome of this situation if political and economic insight cannot win the race against prejudice and ignorance. It is the unhappy fate of the scientist today that he must play the role of Cassandra in the body politic, sending his fellow men to bed with nightmares in the hope to be heard in time.

Fortunately, this second lecture on the "Frontiers of Science" need not be gloomy; on the contrary, it wants to report on developments bright with promise, starting with the apparently naive question: What shall we most reasonably do with our natural resources? In earlier times the answer was simple: here are the materials found in nature and transformed by industry; there are their macro-

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\* Invited paper, "Moving Frontiers of Science" lecture; annual meeting of the American Association for the Advancement of Science, Denver, Colorado, Dec. 26, 1961.

scopic properties, defined and tabulated. Add the practical experience of the engineer and the economic incentive of maximum profit. Into this mold our demands had to fit, rudely deprived of soaring imagination.

Suddenly all this is changing. "Molecular Science" - in decades of quiet studies on electrons, atoms, molecules, and their concerted action in gases, liquids, and solids - has made a more powerful approach possible: "Molecular Engineering," the building of materials and devices to order. We begin to design materials with prescribed properties, to understand the molecular causes of their failings, to build into them safeguards against such failure, and to arrive at true yardsticks of ultimate performance. No longer shackled to presently available materials and characteristics, we are free to dream and find answers to unprecedented challenges. Simultaneously we begin to foresee, in ever widening perspective, the consequences of our actions. About this revolutionary situation, which makes scientists and engineers true allies in a great adventure of the human mind, I would now like to speak, fully aware that most facts here presented are well known to the specialist and that I need your indulgence for trying to unfold a great panorama despite limited insight.

#### The Web of Electron Clouds

When an ultimate Power created protons and electrons, the basic building laws for this world were decided. The two particle types, equipped with equal but opposite elementary electric charges, can hold and neutralize each other electrostatically. Their masses, however, not only exercise gravitational action of the same sign, thus offering no shield against gravitational forces, but the proton is heavier by three orders of magnitude ( $m_+/m_- \simeq 1836$ ). This fact has profound consequences.

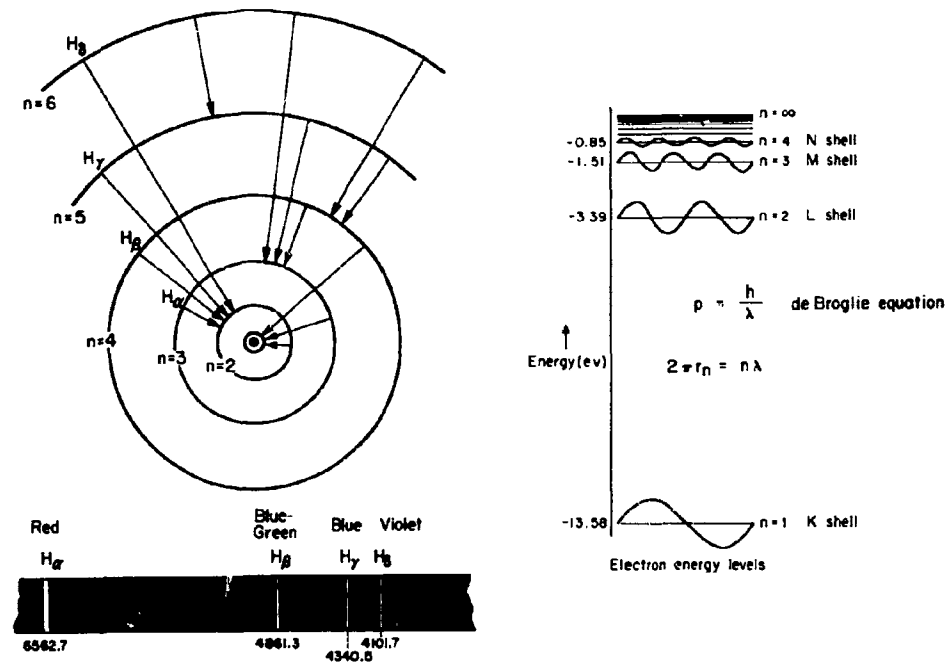


Fig. 1. Standing-wave modes and Bohr orbits of the hydrogen atom.

The accuracy of localizing particles in our space-time framework is proportional to their mass (Heisenberg uncertainty relation). In wave-mechanical language: the wavelength of a particle is inversely proportional to its momentum, hence its mass; the probable whereabouts of particles in stationary states can be described by standing-wave modes of these de Broglie probability waves as solutions of Schrödinger's wave equation (Fig. 1). An electron, trapped by the Coulomb field of a proton in its lowest energy state, is with greatest probability found in a circular Bohr orbit whose circumference equals one wavelength, hence, its radius is inversely proportional to the electron mass. As for any satellite circling the earth, this orbit must have mechanical stability, i. e., the attraction force of the nucleus and the centrifugal force must balance. Thus its average radius for an electron,

trapped by a proton in its ground state, can be calculated as  $r_0 \approx 5.28 \times 10^{-11}$  [m], while for the proton the corresponding radius would be about 1836 times smaller or about  $3 \times 10^{-14}$  [m]. At such small distances, nuclear attraction forces (meson fields) take over and shrink the radius still further. The large gravitational mass ratio of proton to electron thus forces nature to construct atoms from very small positive nuclei surrounded by extended electron clouds.

In addition to charge and mass, electrons and protons have a mechanical angular momentum, a spin; they behave like charged gyroscopes. A rotating charge is akin to a current circling an area; such a ring current produces a magnetic moment ( $\vec{m}$ ) (Fig. 2). The ratio of this moment to the angular momentum ( $\vec{p}'$ ) of the spinning particle is inversely proportional to its mass. Since the mechanical spin of the electron and proton prove to be identical ( $1/2 \hbar$ , where  $\hbar = 2\pi\hbar$  is Planck's constant), the magnetic moment of the electron, known as the Bohr magneton, is about 1836 times larger than the nuclear magneton of the proton.

By increasing the number of protons in the nucleus, the order number, in steps of one and simultaneously adding one electron each to the neutralizing

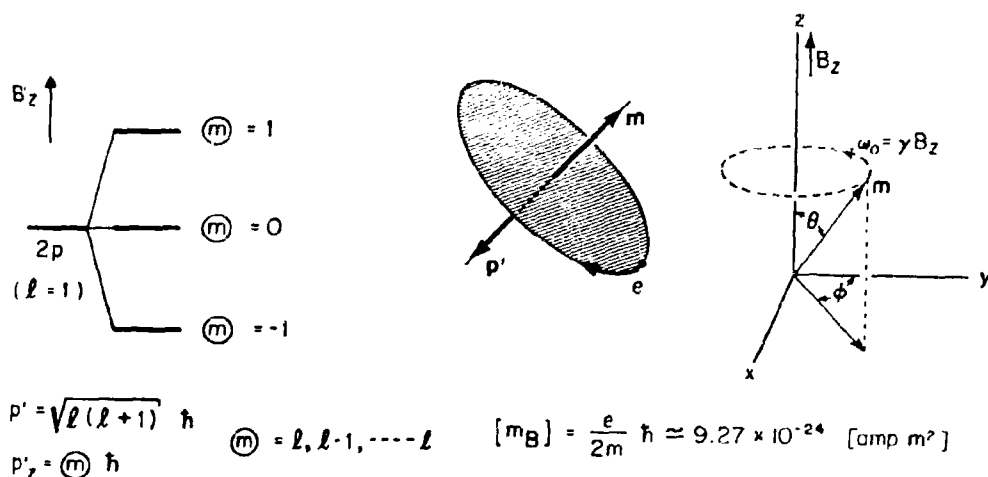


Fig. 2. Orbital electron as a gyroscope.



negative atmosphere, the electrostatic sequence of the atoms of the Periodic System results. (Actually the formation of nuclei proceeds by complicated step reactions; hence, the abundance of elements gives a clue to the conditions prevailing at their creation.<sup>1)</sup>) Intuitively one is inclined to trace back the world with its glorious variety to the specific structure of the nucleus which endows each atom type with a personality of its own. In fact, if we could see with X-ray eyes, the molecular world would appear as an eerie web of electron clouds anchored to positively charged points. These points, examined under much higher magnification, would resolve into spherical potential wells containing, deeply retracted because of their large mass, the nuclei. The actual composition, electric shape, and magnetic moment of these nuclei have only a minor "hyperfine-structure" influence on the electron clouds. The mutual constellation of the nuclear dots in space and the number of positive charges in each dot determine the texture and color of the electron fabric.

Thus, when we understand the electron structure of the atoms and their modes of interaction, we can weave and tear, mend and dye this fabric and thus design materials and devices.

#### Atom Structure

The hydrogen atom, proton and one electron, presents a two-body problem; its possible electron-cloud structures (orbitals) can be calculated accurately, while those of all other atoms - as multibody problems - can only be found by approximation. Thus the results for the H atom have served - rightly or wrongly - as the prototype pattern for all atoms and must be briefly recalled.<sup>2)</sup>

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1) Cf., e.g., J. L. Greenstein, Am. Scientist 49, 449 (1961).

2) Cf., e.g., A. von Hippel, "Molecular Science and Molecular Engineering," The Technology Press of M.I.T. and John Wiley and Sons, New York, 1959.

There is a sequence of stationary energy states, characterized in their average distance from the nucleus by a principal quantum number  $n$ ; its integers  $n = 1, 2, 3, 4, 5, \dots$  can be visualized as designating circular Bohr orbits, in circumference corresponding to  $1, 2, 3, 4, 5, \dots$  electron wavelengths. The ground-state  $n = 1$  represents the deepest trap in which the proton can bind the electron (13.53 ev); all other modes are a succession of excited states. This sequence of extending orbitals causes the shell structure of the atoms (cf. Fig. 1).

The ground state of the hydrogen atom binds the electron in a spherical probability pattern (s state); no direction of rotation is preferred, hence the electron has no orbital angular momentum in reference to the nucleus. For the excited states ( $n > 1$ ) an increasing number of eccentric electron-cloud figurations ( $\ell = n - 1$ ) are also stable solutions of the wave equation; these are characterized by orbital angular momenta  $p' = \sqrt{\ell(\ell + 1)}$ . The azimuthal quantum number  $\ell = 0, 1, 2, 3, 4, \dots$  designates them as s, p, d, f, g,  $\dots$  states, and the integer set  $(n, \ell)$  of two quantum numbers prescribes unambiguously the orbital type (standing-wave mode type) in which the electron finds itself.

It becomes apparent, when placing the hydrogen atom in a magnetic field, that each of these orbital types consists of  $(2\ell + 1)$  individual orbitals. The orbital angular momentum makes the atom a gyroscope and simultaneously creates an orbital magnetic moment (cf. Fig. 2). The external field exercises a torque on the gyroscope by coupling to this magnetic moment; the result is a precession around the field axis. Any recurrent motion in the molecular world characterizes a standing-wave mode; the transition from mode to mode requires a discontinuous, quantized energy step. Hence, the orbital angular momentum must assume discrete, quantized orientations with respect to the field axis; its projection on the field

axis is  $p_z^1 = \textcircled{m} \hbar$ , with the magnetic quantum number  $\textcircled{m}$  ranging from  $\ell$  to  $-\ell$ . Thus each orbital can be designated uniquely by a set of three quantum numbers ( $n, \ell$ , and  $\textcircled{m}$ ).

Finally, an electron placed into an orbital can orient its own angular momentum, its spin component  $s \hbar$ , either parallel or antiparallel to the field ( $s = \pm 1/2$ ); an electron in its orbital is therefore characterized by a set of four quantum numbers ( $n, \ell, \textcircled{m}, s$ ). Pauli's exclusion principle requires that particles with half-integer spins like the electron must be distinguishable each by its own set of four quantum numbers; that is, such particles obey Fermi-Dirac statistics. Each atomic orbital can thus only accept two electrons paired with antiparallel spins.

The Periodic System as presented in Fig. 3 assumes that the multi-electron systems of the atoms can be described by hydrogenlike orbitals. We have the various shells ( $n$ ) and subshells ( $\ell$ ) of orbital type  $s, p, d, f, g, \dots$ . Since an orbital can accommodate 2 electrons and each orbital type has  $2\ell + 1$  orbitals, the subshells are filled when containing  $2(2\ell + 1)$  or 2, 6, 10, 14, 18,  $\dots$  electrons respectively. The electron distribution of an atom can be written in shorthand by giving the integer number of the shell, the letter of the subshell, and above it the number of occupying electrons as superscript; for example, the electron distribution in the Fe atom (order number 26) is represented unambiguously by the symbol  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ .

Here appears our first predicament: only experiment can clarify that the 3d subshell takes in six electrons, leaving two in the 4s orbitals. The sudden filling of inner d and f subshells shown in Fig. 3 certifies that the mutual energy relations between shells and subshells change with occupation. Furthermore we can foresee that the energy states, especially those of the outer shells, will be altered by interaction with the surroundings.

n ↓	1	Ia	1	IIa	2	VIIb	2												
1		H				He													
2		Li	Be																
3		Na	Mg	IIIa	IVa	Va	VIa	VIIa	VIII	IB	IIB	IIIb	IVb	Vb	VIb	VIIb	He		
4		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5		Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6		Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7		Fr	Ra	Ac															
		s		d										p					
4f				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
5f				Ac	Th	Pa	U	Np	Am	Pu	Cm	Bk	Cf	Es	Fm	Md	No	Lw	
				f															

Fig. 3. Periodic system based on hydrogenlike orbitals.

Nature designs everything from atoms; hence, we should be able to design any kind of material with foresight if we thoroughly understood the Periodic System in all its implications. At this stage - like weather forecasters - we are still members of the gambling profession.

### Elements and Compounds

Atoms are not the inert building stones of fixed size, shape, and connecting links that a model designer has to pretend. Isolated, they appear spherical and may be described by some nearest-approach distance: an atomic radius (when neutral) or positive and negative ionic radii (when they shed or trap electrons). However, the distortion of electron clouds by approaching neighbors creates polarity, ranging all the way from a weak van der Waals attraction by fluctuating dipole moments - caused by phase relations between electrons of

interacting clouds that try to avoid each other - to the strong permanent dipole moments of polar molecules. Furthermore, atoms are inherently endowed by their eccentric electron clouds with strong stereoproperties. Hence, the valence electrons of unfilled outer shells form strong directive links (ligands) to their neighbors.

Gilbert N. Lewis first recognized the electron-pair bond which allows the  $1s^1$  electrons of two hydrogen atoms to pair in antiparallel spin orientation, forming  $H_2$ , or alkali halide molecules to acquire the octet structure  $s^2p^6$  of rare gas atoms. Obviously, the originally spherical electron distribution has been drastically altered by such diatomic molecule formation to the cylindrical symmetry of dinuclear systems. The overlap of the previously isolated electron clouds becomes a measure of the bond strength. The valence electrons have been saturated, nearly equally strong diatomic molecules  $H_2$  or NaCl formed (ca. 103 and 97 kcal/mole respectively), and one might expect that such molecules will behave inert like rare gas atoms.

Rare gases cannot form directed bonds as long as their saturated spherical electron-cloud system remains unbroken by excitation. Hence only the weak van der Waals attraction acts and packs the atoms as equal spheres, like oranges in crates, in one of two densely packed arrays (Fig. 4): in planes with repeat sequence ABAB... or ABCABC..., yielding hexagonal or face-centered cubic crystals, respectively. In both cases each atom is surrounded by twelve neighbors at equal distances (coordination number CN = 12). Very low melting and boiling points result, indicating with their rising trend from He to Rn that the cohesion increases with the number of participating electrons (Fig. 5).

$H_2$  acts according to expectation: The hydrogen molecules pack as densely as possible by van der Waals forces without losing their identity; melting and boiling points are low. The individual alkali halide molecules, in contrast, by

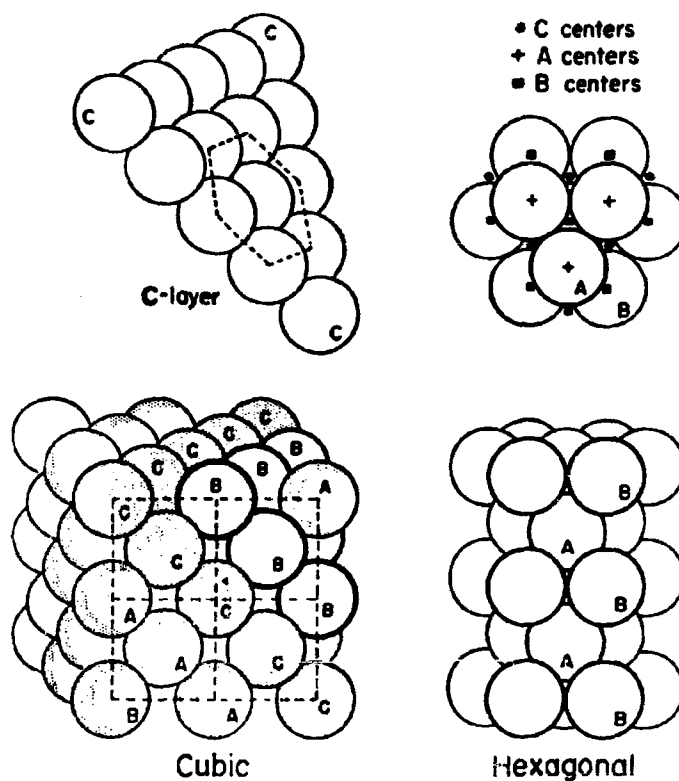


Fig. 4.  
Close-packed arrays  
of spheres.

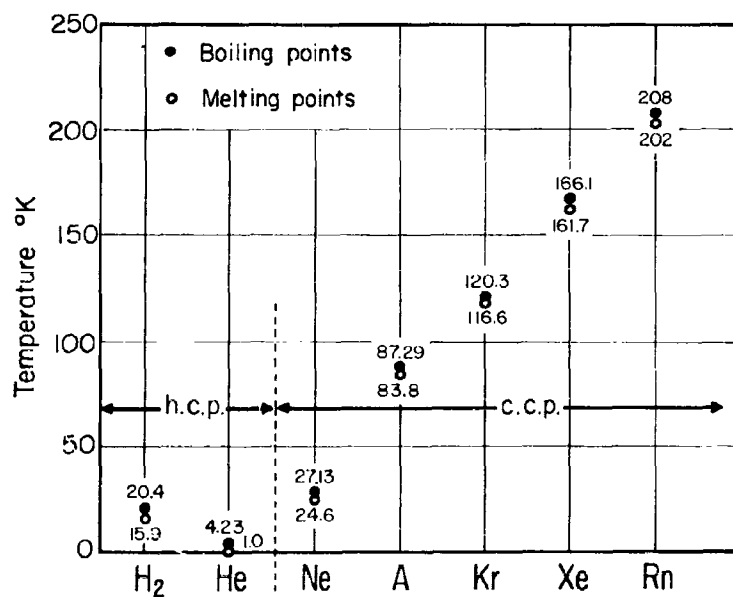


Fig. 5.  
Melting and boiling  
points of H<sub>2</sub> and  
the rare gases.

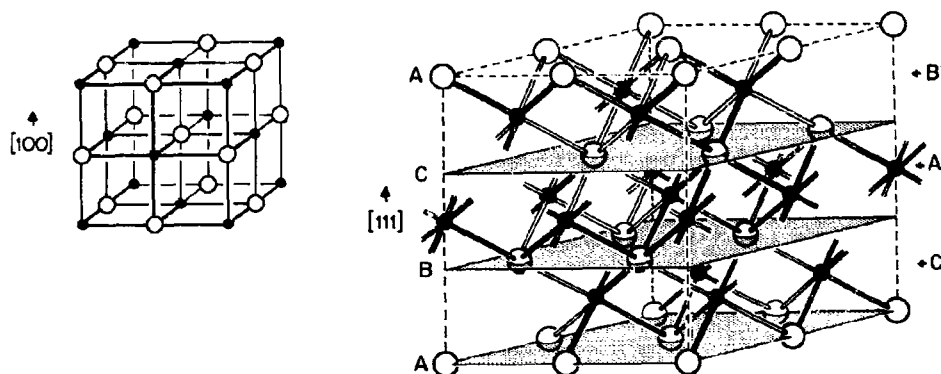


Fig. 6. Rock salt structure as related to close-packed structure.

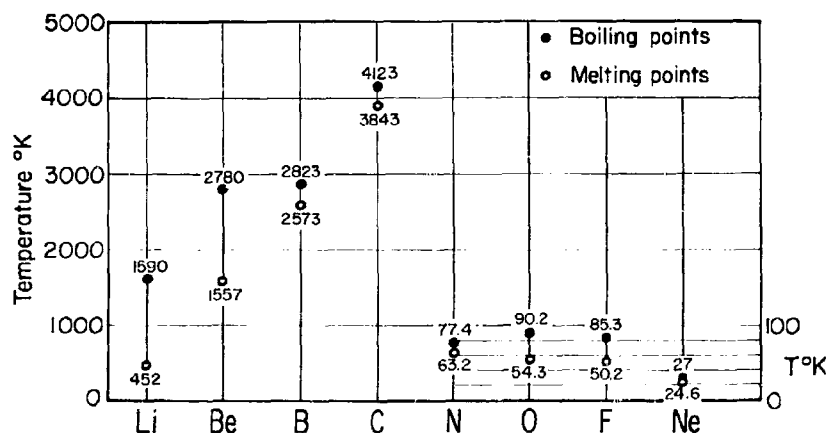


Fig. 7. Melting and boiling points for the elements of the second row.

condensing lose their identity; they are dissolved - with large energy release - in the ionic rock salt structure. Still, there is a memory left of the rare gas behavior when this structure is properly drawn:  $\text{Na}^+$  and  $\text{Cl}^-$  separately have rare gas shells and form two interleaving sublattices of the cubic close-packed type (Fig. 6).

Turning to the second row of the Periodic System we may predict that lithium and boron, with a lone  $2s^1$  and  $2p^1$  electron respectively, will form  $\text{Li}_2$  and  $\text{B}_2$  molecules in analogy to  $\text{H}_2$  and that Be with its  $2s^2$  electron pair remains monatomic like a rare gas atom. This is about true, but instead of

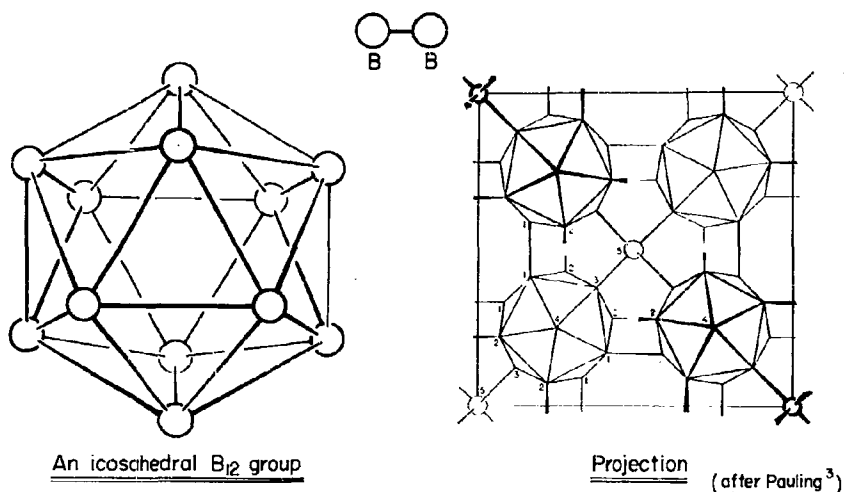


Fig. 8. The structure of boron.

condensing into insulating liquids at low temperature, Li and Be become metals and B a semiconductor. Melting and boiling points (Fig. 7) rise high, and only from nitrogen on is the rare gas behavior resumed by diatomic molecules (as in the case of  $H_2$ ).

That alkali atoms form metals might have been surmised by their tendency in the alkali halides to regain their rare gas shell by shedding the lone electron. Thus the fixed anion sublattice in Fig. 6 can be visualized as being replaced by a mobile electron lattice. The fact that the alkaline-earth atoms share their two electrons in metallic bonding is an extension of this situation. However, the structure of the boron crystal is a complete surprise: its tetragonal unit cell contains four icosahedra of 12 atoms each with ligancy 6 and two interstitial B atoms of ligancy 4 that knit these regular polyhedra together (Fig. 8).<sup>3)</sup> Thus the boron atom with its three valence electrons can contribute only a fractional electron charge to its six or four bonds, respectively.

Obviously, the concept of clamping atoms together with their hydrogen-

3) Cf. L. Pauling, "The Nature of the Chemical Bond," 3rd edition, Cornell University Press, Ithaca, N. Y., 1960.



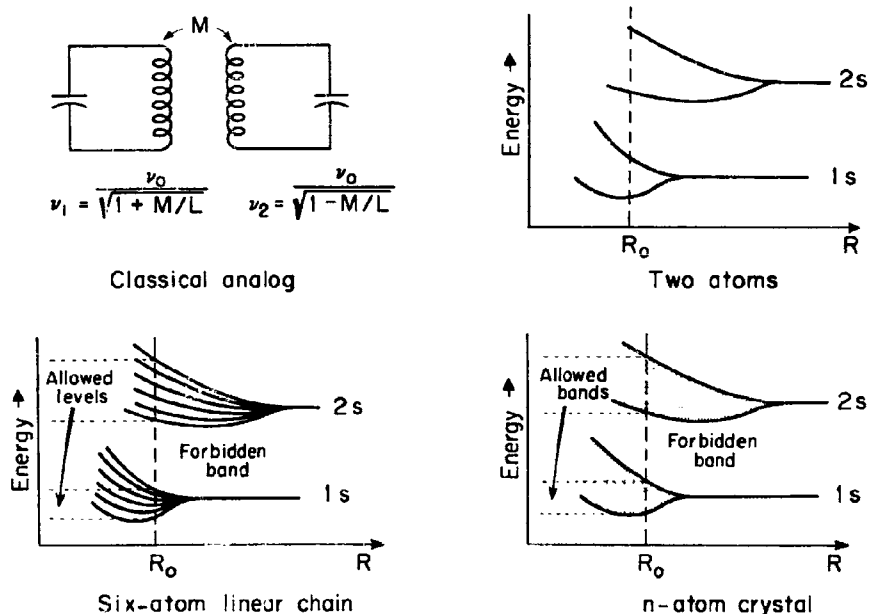


Fig. 9. Coupling of classical oscillators and band structure of crystals.

like s, p, d, ... orbitals in pair-bond formation, thereby saturating valencies and then packing tightly, does not suffice. We have neglected the fact that the electron-density patterns assigned to each standing-wave mode actually spread over all space. Hence coupling must occur between all mutually compatible electron modes inside atoms as well as between neighbors. Such coupling is well known in the case of classical oscillators and splits a resonant mode into a higher and a lower frequency band (Fig. 9). Similarly, the individual energy states of atoms split: (a) within the atoms themselves, by magnetic coupling of orbital and spin moments (internal Zeeman effects) and by electrostatic interaction (internal Stark effects); (b) through external interactions with neighboring atoms, again by coupling of orbital and spin momenta and by reacting to electrostatic effects (e.g., the crystal fields of solids).

One simple outcome of this splitting of energy states is the well-known

Bloch-Wilson model classifying crystals as insulators, semiconductors, or metals according to the separation or overlap of the energy bands in which electrons or holes may transfer through a periodic lattice structure. Much ingenious work is at present devoted to the elucidation of the actual stereo-structure of such bands as seen from the standpoint of electrons and their wavelengths (i. e., in  $k$  space).<sup>4)</sup>

A second result of the coupling of wave modes is that combinations of such modes can be excited like the timbre of a musical instrument. In simple cases only two wave-function types may dominantly be involved, as in the celebrated s-p hybridization of the carbon atom, which starts organic chemistry on its way with aliphatic and aromatic compounds (Fig. 10). Here pair-bonds still suffice, but the structure of boron (cf. Fig. 8) makes it obvious that individual electrons may spread themselves over various compatible wave modes. Thus the actual structure can be visualized as containing genes of a variety of individual constellations, each making its contribution to the structure, properties, and cohesive strength of the final array. This is the concept of quantum-mechanical resonance, used so successfully by Pauling<sup>3)</sup> in describing the nature of the chemical bond.

#### Molecules and Crystals

Such latent properties of electron-cloud formation, called to the fore as the environment dictates, makes designing with atoms an occupation filled with curious anticipation, like gardening in a greenhouse: select the seeds, set the conditions of the surroundings, and things begin to happen.

Three extreme cases became apparent in the preceding discussion:

(a) Atoms may stay single in the gaseous phase because they are inert (rare

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4) Cf., e. g., J. C. Slater, "The Electronic Structure of Solids," in Handbuch der Physik, Vol. 19, Springer, Berlin, 1956, p. 1.

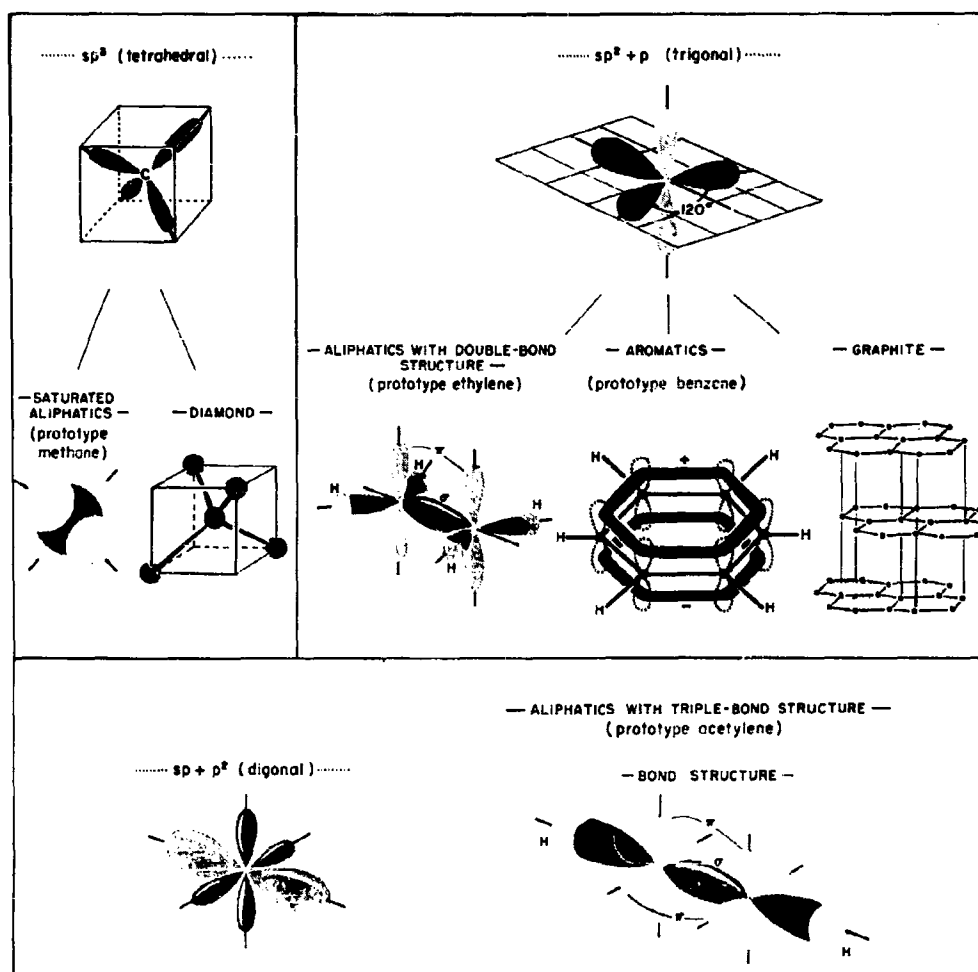


Fig. 10. Hybrid bonds of carbon.

gases) or they may form semi-inert molecules by saturation of primary valence bonds (e.g.,  $H_2$ ). Weak secondary attraction condenses these entities into close-packed phases without destroying their identity; low melting and boiling points result (cf. Figs. 5 and 7). (b) Atoms stay single in the gaseous phase (e.g., Be), because strong primary bonds develop only in multiatomic clusters where common wave functions can bind the array; an electron community arises, usually leading to the metallic state. This is a very

common situation, since three quarters of all elements are metals; higher melting and/or boiling points and monatomic vapors are the rule. (c) Molecules form in the gaseous state by valence bonding but are torn to pieces by stronger primary bonds of the condensed phases. The reason may be the polarity of the molecule, leading to the far-ranging Coulomb fields of an ionic lattice structure (e.g., NaCl, cf. Fig. 6).











$r_c / r_a$	CN	Type of site	
0.155 ↔ 0.255	3	 Triangular	
0.255 ↔ 0.414	4	 Tetrahedral	
0.414 ↔ 0.732	6	 Octahedral	
0.732 ↔ 1.00	8	 Cubic	
1.00	12	 Densest packed	

Fig. 11. Radius ratio and coordination.

It may be the community of metal electrons that dissolves the molecule as in the case of  $\text{Li}_2$ , or covalent links between nearest neighbors may in continuous sequence build strong three-dimensional networks as in diamond, two-dimensional planes as in graphite, or linear chains stretching through space as in carbon polymers (cf. Fig. 10).

In their extreme form, metallic and ionic bonds act compacting according to the principle "horror vacui," and tend to fill space as densely as the radius ratio of the partners permits (Fig. 11). In contrast, the short-ranging, strongly directive covalent bonds are the primary tools of imaginative architecture. Actually, this distinction is blurred in nature, because any bond between unlike atoms imparts polarity; even shared electron clouds can move in cooperative polarity against the residual structure.

The diversity of nature stemming from the various bonding possibilities

of more than a hundred atoms would be staggering even if the structure of a material were determined uniquely by temperature and chemical composition. Actually, as everyone knows when ordering his egg boiled, fried, or scrambled, there often are multiple choices in arranging the same elementary constituents. Prehistory enters for samples as for living beings to codetermine their present state.

In its simplest form, this prehistory dependence becomes apparent in the polymorphism of elements. Oxygen gas, for example, consists normally of  $O=O$  molecules, because the double bond is stronger than two single bonds; sulfur and selenium vapor, on the other hand, tend to contain  $S_8$  or  $Se_8$  ring molecules, because two single bonds are stronger than one double bond (Fig. 12). The double bond, however, is still much stronger than one single bond; hence, the composition of the vapor phase changes with increasing temperature from eight-membered rings to diatomic molecules. When the ring molecules break open, the possibility of chain polymerization arises, as is well known from the formation of plastic sulfur. At room temperature this material reverts to the brittle ring structure, but selenium occurs in stable crystals built from rings or chains and also in amorphous chain-polymer modifications. In the ring form, selenium is an insulator, in the chain form a semiconductor, since electron defects can be transferred along the chains. When

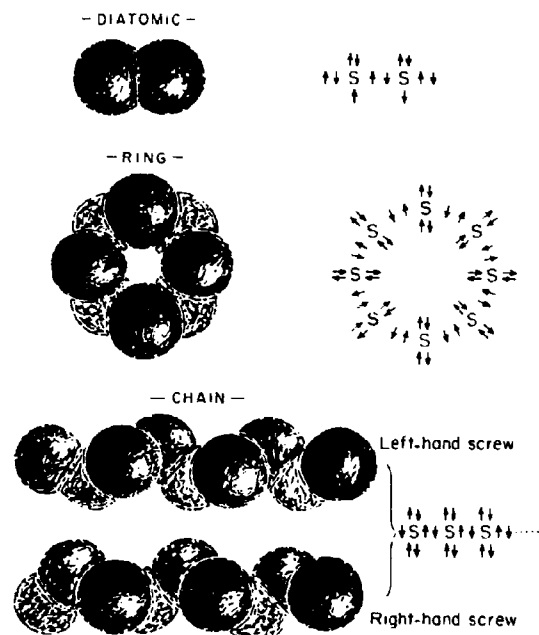


Fig. 12. Various types of sulfur molecules.

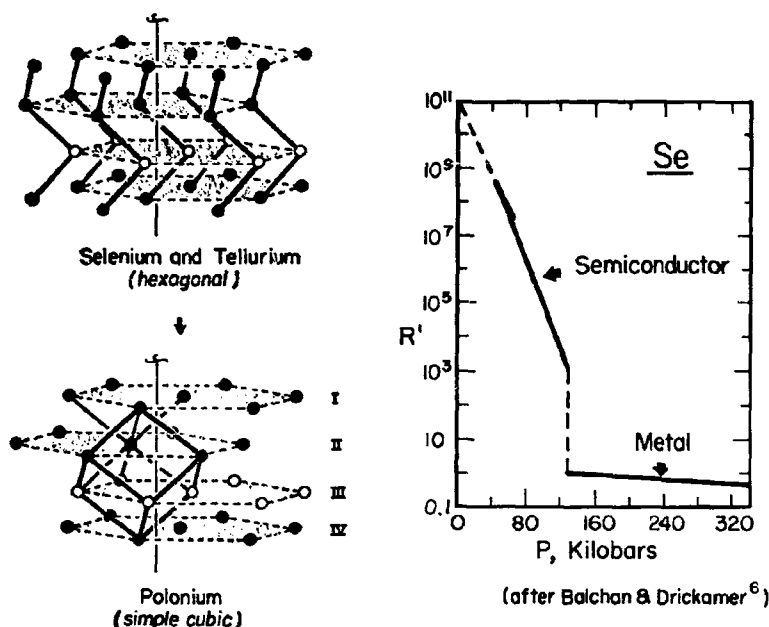


Fig. 13.  
Selenium-to polonium-  
type transition.

squeezed by very high pressure - as might be expected from the structure relation to Te and the metal Po<sup>5)</sup> - Se becomes a metal (Fig. 13).<sup>6)</sup>

Since high temperature breaks down pre-existing molecular entities and high pressure holds the constituents at effective interaction distance, high-pressure, high-temperature techniques gain increasing importance for synthesizing modifications normally precluded by interfering bond formations. The synthesis of diamond, of boron nitride in diamond instead of graphite structure, and of the new SiO<sub>2</sub> modification coesite - proving so useful for the geologist in identifying craters of meteoric origin - are outstanding accomplishments of this approach.<sup>7)</sup> Synthesizing materials from defined elementary particles by molecular-beam techniques in ultrahigh vacuum is another promising method still in

5) A. von Hippel, J. Chem. Phys. 16, 372 (1948)

6) A.S. Balchan and H.G. Drickamer, *ibid.* 34, 1948 (1961).

7) Cf. Proc. Internatl. Conference on High Pressure Research, F.P. Bundy, W.R. Hibbard, Jr., and H.M. Strong, Eds., John Wiley and Sons, New York, 1961.

its pioneering stages.

Allotropy and the existence of competing structure types lead automatically to the subject of phase transitions. With falling temperature a material normally contracts, overlap and interaction time between electron clouds increases, and randomizing thermal agitation subsides. Thus, crystals at high temperature tend to be more symmetrical and tolerant for substitutions, while in cooling the weaker, more specific interaction forces emerge from the sea of thermal noise and enforce special types of order, thereby lowering the crystal symmetry. If this reorganization is incompatible with the pre-existing lattice and the new arrangement can nucleate, the sample will shatter and recrystallize in a first-order transition. On the other hand, a completely continuous transformation may be possible, as well known from the disorder  $\longleftrightarrow$  order transitions of the constituents of alloys, the magnetic moments of electrons forming the spin systems of ferro- and antiferromagnetics or the electric moments of polar crystals organizing in dipole chains of piezo- and ferroelectrics.<sup>2)</sup> The time taken by such phase transitions may range all the way from instantaneous explosion or thermal hysteresis of nanoseconds duration to the millions of years traceable in geological strata.

Competing types of order are of decisive importance in the organic world. Whether polyisoprene assumes the cis or trans structure, decides whether a useful elastic rubber or an inelastic balata is obtained (Fig. 14). The ordering of water molecules twists protein molecules into spiral structures decisive for life processes,<sup>8)</sup> and here again the differentiation into right-hand or left-hand screw structures is vital for the activation of such processes.

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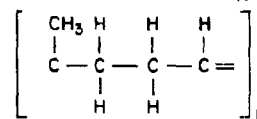
8) Cf. "The Living Cell," Sci. American 205, No. 9 (1961).

# Laws of Molecular Architecture

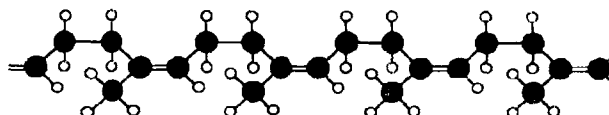
A great variety of individual design concepts have appeared in the preceding discussion: hydrogenlike wave functions of atoms and electron-pair bonding; modifications of simple atomic orbitals by hybridization; combinations described by quantum-mechanical resonance; splitting of energy states by coupling, leading to molecular orbitals and the band structure of crystals; dense packing, as far as radii and their ratio allow; molecular, ionic, covalent, and metallic structures; polarity, polymorphism, and isomers; phase transitions and the importance of prehistory. Sparked by magnetic-resonance techniques and developments such as masers and lasers, more and more becomes known about the fine structure of energy states; and the introduction of increasingly powerful computers allows the calculation of wave functions with rapidly improving reliability. We learn, but a nightmarish feeling begins to assail the scientist of becoming lost in the labyrinth of Minotaur. Where are the guiding principles that can lead through this maze of phenomena in graphic understanding?

At the outset we stated that the space correlation and charge of the nuclei are the primary determinants for the web of electron clouds; hence, topology should be a guide. Judged from this point of view the structures

Polyisoprene  $[C_5H_8]_n$



NATURAL RUBBER  
(elastic cis form)



GUTTA-PERCHA  
(slightly elastic trans form)

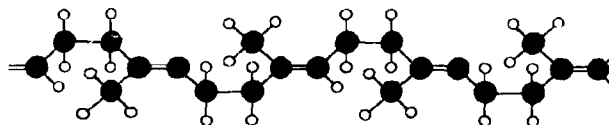
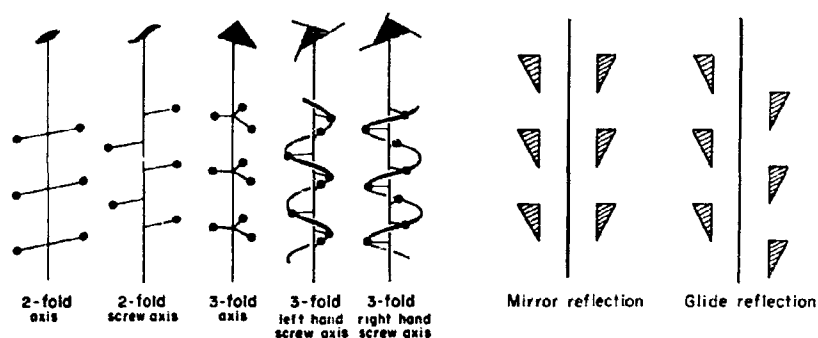


Fig. 14. Stereoisomerism of polyisoprene.





Axes and screw axes
Reflection and glide reflection planes

Fig. 15. Various types of symmetry elements.

of molecules and crystals are characterized by the presence (or absence) of certain elements of symmetry: a center of symmetry, planes of reflection or glide reflection, and axes of rotation and screw rotation (Fig. 15). For crystals the stringent requirement of periodic repetition of lattice points limits the admissible periodicity in rotation to 1, 2, 3, 4, and 6-fold axes and with it the possible number of space groups to 230. Structure analysis can assign any crystal to one of these 230 compartments.

This type of classification, based on inherent symmetry properties, is more exact than the Linnaean system, which orders the world of plants, but equally uninformative. We seek elucidation of the type provided by Darwin's "Origin of Species": What kind of structures are chosen for molecular reasons? Which rules guide their design and assure stability, i. e., "survival of the fittest?"

Answers to these questions begin to evolve, but will often not be unique, because a variety of molecular causes can hide behind the same macroscopic phenomenon. For example, violation of the just stated rule that the long-range periodic order of crystalline networks permits only

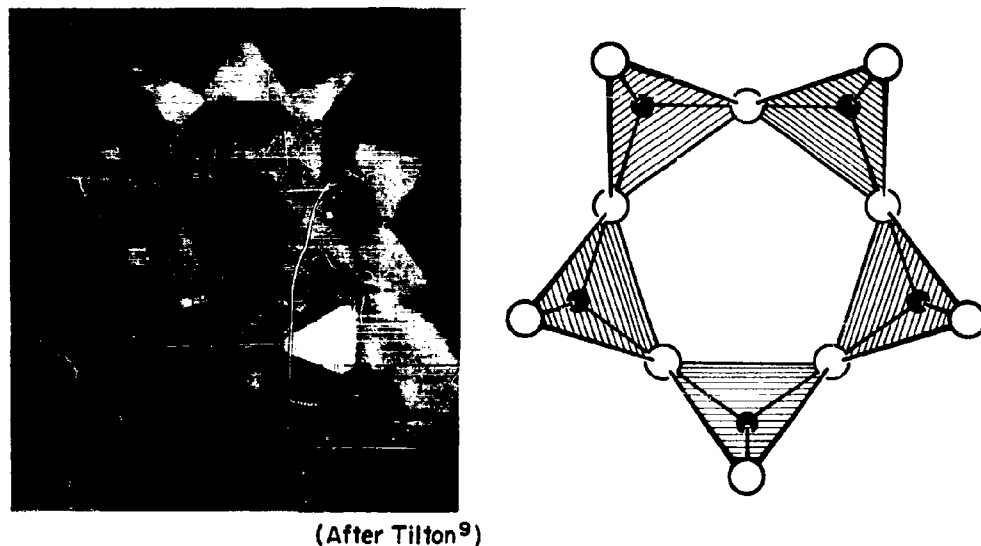


Fig. 16. Pentagonal dodecahedral groups in silicate glass or water.

1, 2, 3, 4, and 6-fold axes of rotation should allow forcing materials into the glassy state of short-range order. This has been suggested years ago by Tilton,<sup>9)</sup> who, in building models of silicates, demonstrated the likely occurrence of groups with 5-fold axes; and a very similar kind of arrangement has been invoked by Pauling for explaining the hydrogen-bonded structure of water (Fig. 16). On the other hand, the symmetry of molecular groups need not transfer to a crystal structure, as is demonstrated by boron, whose icosahedra of 5-fold rotation symmetry are safely tucked away in a unit cell of tetragonal symmetry (cf. Fig. 8), or by virus particles with 5-fold axes assembled in a close-packed crystal structure.

There are other causes for glass formation; the competition of various molecular constellations on the basis of nearly equal probability as, e.g., in borosilicates, where  $B^{3+}$  can enter either in triangular or tetrahedral bonding

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9) L. W. Tilton, J. Research Natl. Bur. Standards 59, 139 (1957).

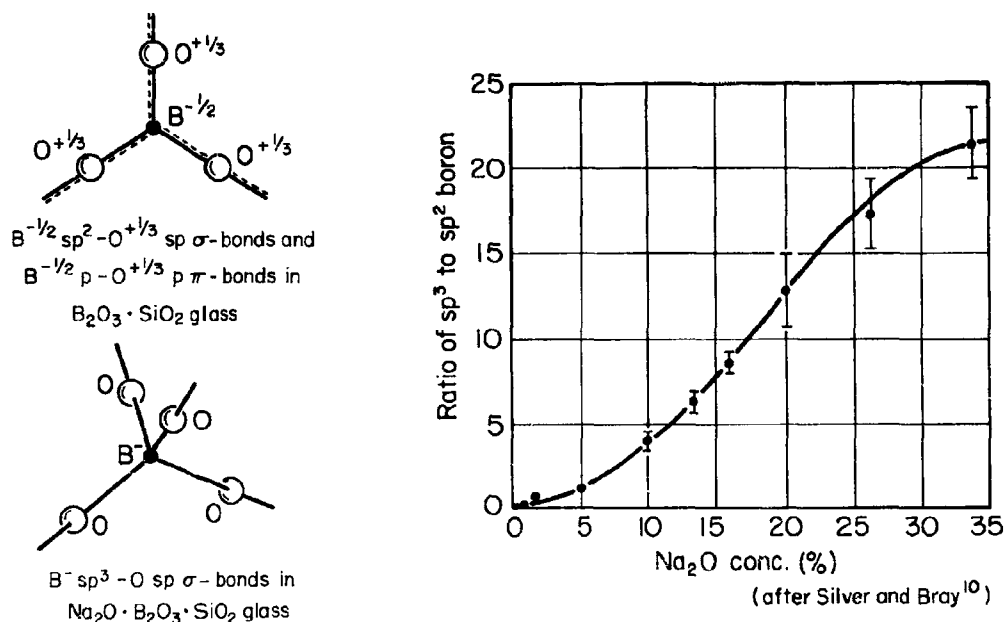


Fig. 17. Competing coordinations of  $B^{3+}$  in sodium borosilicates.

as demonstrated by Warren and Bray (Fig. 17);<sup>10)</sup> the agglomeration of chain molecules to glassy polymer structures; or the freezing-in of amorphous structures through suppression of nucleation. By developing crystal nuclei afterwards in glass systems, Stookey<sup>11)</sup> pioneered the new pyroceramics, materials that combine the strength of crystalline with the bounce of amorphous regions (Fig. 18) - a trick used by nature in the growing of trees and the formation of muscle fibers.

Returning once more to molecular design, the recent spurt in the recognition of polyhedra molecules has made it clear that practically any structure which seems topologically reasonable can be made, and that increased symmetry

10) J. Biscoe and B. E. Warren, J. Am. Chem. Soc. 21, 287 (1938); A.H. Silver and P. J. Bray, J. Chem. Phys. 29, 984 (1958).

11) S.D. Stookey, "Ceramic Fabrication Processes," W.D. Kingery, Ed., Technical Press of Massachusetts Institute of Technology and John Wiley and Sons, New York, 1958, p. 189.

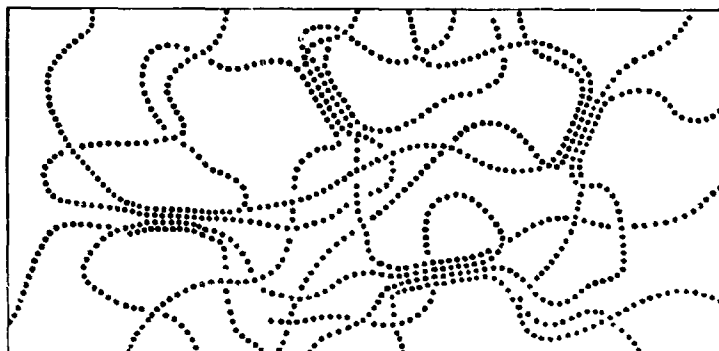


Fig. 18.

Combination of amorphous and crystalline regions.

(*ceteris paribus*) imparts increased stability. A good example is the sequence of boron hydride molecules studied by Lipscomb and co-workers.<sup>12)</sup> The regular icosahedral molecule  $[B_{12}H_{12}]^{2-}$  (Fig. 19) proved so stable that it could be injected into a patient in large doses for cancer treatment by neutron bombardment, while the semifinished  $B_{10}H_{14}$  structure would have been broken down in the body of the victim, causing his speedy demise.

The designing of materials could start with molecular topology: tentative selections of the space arrangement of nuclei would prescribe the symmetry conditions - formulated by group theory - to which the system of interlinking electron clouds is subjected. Recourse to two types of restrictions, "Tolerance Conditions" and "Property Conditions," would then lead systematically to alterations in the proposed array and to specific choices in the selection of nuclei. The procedure is akin to that of an architect who sketchily outlines a building and then - by carefully considering the restrictions imposed on his phantasy by the mechanical stability and function of the structure - arrives at choices of final design.

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12) W. N. Lipscomb, "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeléus and A. G. Sharpe, Eds., Vol. 1, Academic Press, New York, 1959, p. 117; W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, J. Am. Chem. Soc. 81, 5833 (1959); J. A. Wunderlich and W. N. Lipscomb, *ibid.* 82, 4427 (1960); E. B. More, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, J. Chem. Phys. 35, 1329 (1961).

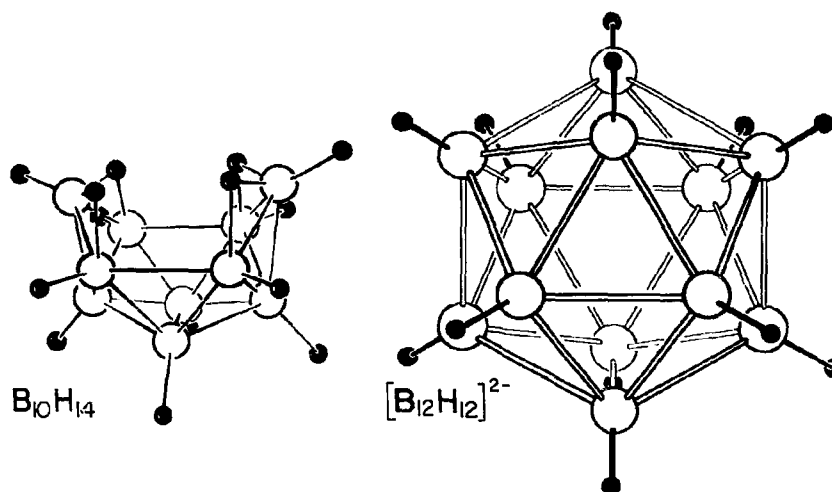


Fig. 19. Polyhedral molecules of boron hydrides.

Tolerance conditions for a proposed structure are of molecular origin and specify the limits in which alterations in charge distribution and distortions of the space arrangement are permissible without causing instability. Property conditions, in contrast, originate as macroscopic specifications for the performance of a material or device and have to be translated into molecular prescriptions.

Figure 20 illustrates the action of tolerance conditions: Carbon atoms (group IV of the Periodic System, Fig. 3) can be replaced by 50% each of boron atoms (group III) and of nitrogen atoms (group V) without destroying the structure of the benzene ring or the diamond lattice. Here the electron-cloud structure can average over the nuclear charge distribution. However, if we try to stretch the limits of symmetrical replacement further by introducing the atoms beryllium (group II) and oxygen (group VI) instead of boron and nitrogen, the benzene ring equivalent  $Be_3O_3$  does not form and the BeO crystal does not derive from the diamond structure.

A comparison of the two crystal types, BN and BeO, yields more information (Fig. 21): The diamond lattice, when composed of two different types of atoms, is identical with the sphalerite structure (zinc blende), the BeO lattice with the wurtzite structure of ZnS. The former can be derived from two interpenetrating cubic close-packed lattices, the latter from two hexagonal ones. Hence, by increasing the polarity of the

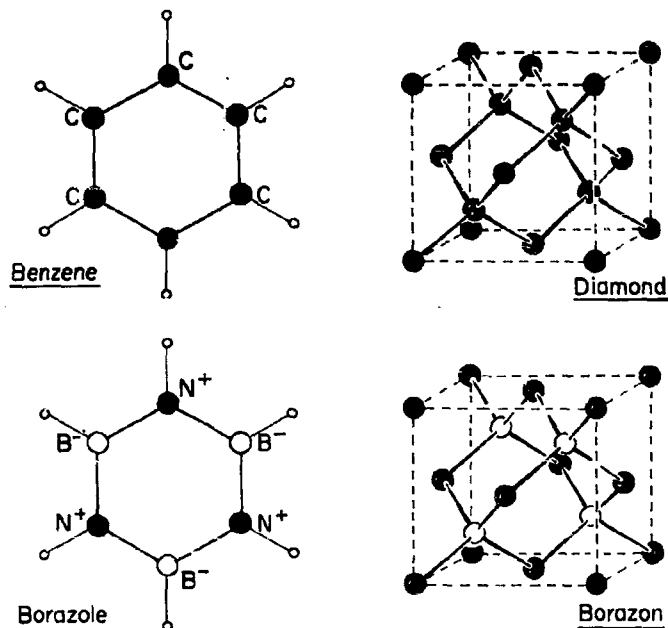


Fig. 20. Structure preservation by averaging nuclear charges.

array, we have unbalanced the sphalerite in favor of the wurtzite arrangement.

In both situations each atom type is tetrahedrally bonded to the other (CN4),

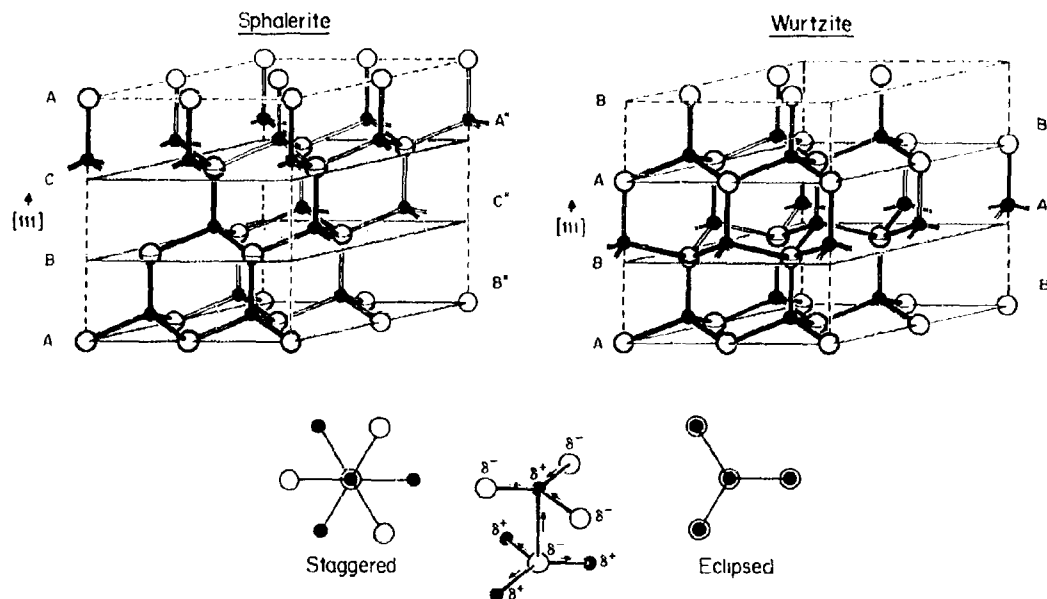


Fig. 21. ZnS-type structure.

but - viewed in the [111] direction - subsequent tetrahedra in sphalerite are staggered and in wurtzite, eclipsed. The staggered array allows better space accommodation, the eclipsed array a closer bonding of opposite charges; this explains the transformation observed.

The extreme step in polar substitution is balancing of lithium (group I) against fluorine (group VII). This wipes out the tetrahedral (CN4) organization of the ZnS lattices in favor of the octahedral (CN6) coordination of the rock salt structure. The change has been enforced by the increase in radius ratio of cation to anion ( $r_c/r_a$  for  $\text{Be}^{2+}/\text{O}^{2-} = 0.25$ , for  $\text{Li}^+/\text{F}^- = 0.52$ ) as expected from Fig. 11. Still, like the sphalerite structure of BN, the rock salt structure of LiF can be derived from two interpenetrating cubic close-packed sublattices (cf. Fig. 6).

This switching between crystal types (derived from close-packed arrays) at the command of tolerance conditions concerned with polarity and space accommodation, invites clarification of the kinship of such types. Insight is provided by viewing the interstitial space arrangement for the close-packed structures of Fig. 4. This space is partitioned into interlocking tetrahedral and octahedral compartments (Fig. 22); a lattice section of  $n$  atoms contains  $n$  octahedral and  $2n$  tetrahedral sites. The centers of the octahedra lie halfway between the layers of the original lattice, those of the tetrahedra at  $1/4$  and  $3/4$  of the spacing. (A model design with transparent tetrahedral and octahedral building blocks has recently been perfected by A. Loeb in connection with his imaginative approach to a new crystal algebra.<sup>13)</sup>)

Starting with a cubic face-centered array of layer sequence ABCABC..., we arrive at the rock salt structure by occupation of all the octahedral inter-

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13) A. L. Loeb, *Acta Cryst.* 11, 469 (1958); I. L. Morris and A. L. Loeb, *ibid.* 13, 434 (1960).

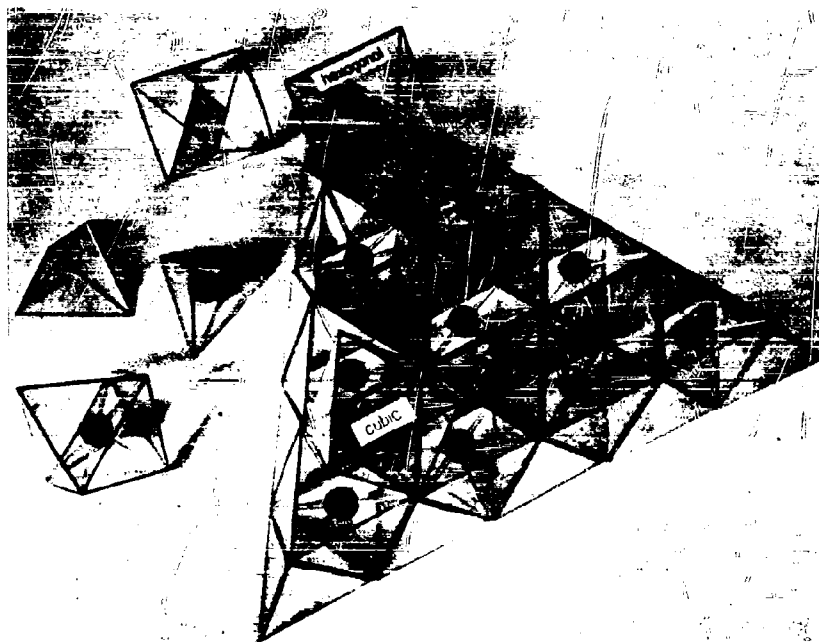


Fig. 22. Close-packed structures built from interstitial tetrahedra and octahedra.

stitial sites (cf. Fig. 6) or at the sphalerite structure by filling all tetrahedral sites in either the  $1/4$  or the  $3/4$  location. By choosing the hexagonal close packing with layer sequence ABAB... and occupying one of the two sets of tetrahedral sites, the wurtzite structure is created (cf. Fig. 21). Since the centers of the octahedra lie midway between the original layers, the spacing between the positive and negative planes of the rock salt structure is uniform and the crystal has a center of symmetry. For the tetrahedrally bonded sphalerite and wurtzite, on the other hand, the occupation of the  $1/4$  or  $3/4$  center positions causes a periodic bunching of the charged planes; the center of symmetry is destroyed.

#### Structure and Properties

Such topological differences in competing arrangements should produce



profound property changes. Indeed, crystals of the rock salt structure remain electrically neutral under mechanical stress; insulators of the sphalerite type react piezoelectrically; i. e., they create potential differences of opposite signs on tension and compression; while those of the wurtzite type are in addition pyroelectric; i. e., potential differences of opposite signs develop also on heating and cooling. Thus both tetrahedrally bonded polar crystal types can serve as electromechanical transducers and the wurtzite type in addition as a thermosensing device.

For molecular interpretation of these phenomena, the ions of opposite polarity can be visualized as forming a network of permanent dipole moments. In the rock salt structure the neutralizing balance of these moments cannot be upset by mechanical distortion; in sphalerite it can, and in wurtzite it does not exist a priori, because the moments do not cancel but create a polar axis.

The polar double-layer structure produces additional differences between the  $[111]$  and  $[\bar{1}\bar{1}\bar{1}]$  directions in sphalerite, and the  $[001]$  and  $[00\bar{1}]$  directions in wurtzite; the X-ray scattering is unlike in the two opposite directions and since the crystals terminate on the one side with a cation and on the other with an anion layer, the electrochemical potentials and etching properties of these end surfaces are quite dissimilar (Fig. 23).<sup>14)</sup> By combining sphalerite and wurtzite in twinned arrays, high-voltage photocells can be produced.<sup>15)</sup>

The structure transformation observed for the sequence of insulators  $C \rightarrow BN \rightarrow BeO \rightarrow LiF$  in the second row of the Periodic System repeats itself for the b elements of the higher rows (Si, Ge, and gray Sn) in the corresponding III-V,<sup>16)</sup>

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14) H. C. Gatos, "Surface Chemistry of Metals and Semiconductors," John Wiley and Sons, New York, 1960, p. 399.

15) W. J. Merz, *Helv. Phys. Acta* 31, 625 (1958).

16) H. Welker and H. Weiss, "Group III - Group V Compounds," in *Solid State Physics*, Vol. 3, F. Seitz and D. Turnbull, Eds., Academic Press, New York, 1956, p. 1.

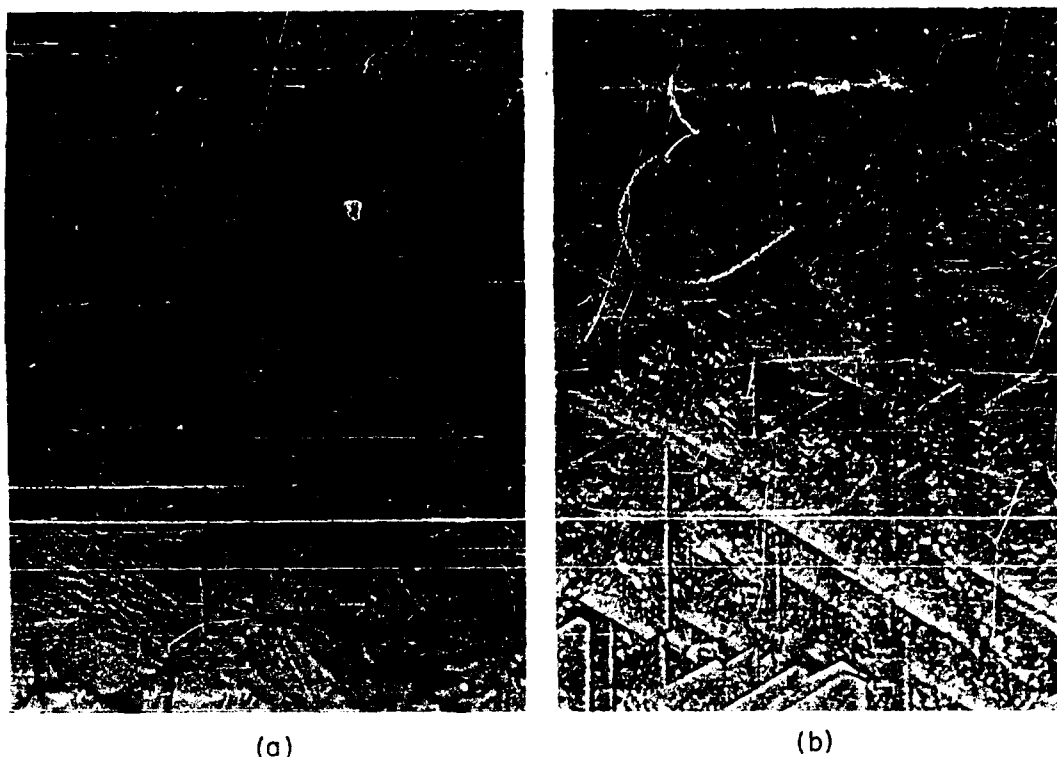


Fig. 23.  $\{111\}$  surfaces of InSb etched for 30 minutes at  $80^{\circ}\text{C}$  ( $0.2\text{ N Fe}^{3+}$  in  $6\text{ N HCl}$ ) (300X): (a) indium surface, (b) antimony surface. (After Gatos.<sup>14)</sup>)

II-VI, and I-VII compounds.<sup>17)</sup> These elements and compounds are the decisive semiconductor materials for transistors and solid-state diodes, for thermoelectric converters, and for solar-energy photocells. Here the band structure, the gap width between valence and conduction band, the mass and mobility of electrons and holes can be adjusted by composition changes, and charge carriers can be mobilized by cation substitution in minute quantities (doping). An impressive amount of fundamental molecular-science knowledge has been gathered rapidly about these materials under the impact of molecular-engineering applications.<sup>17)</sup>

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17) Cf., e.g., "Semiconductors," N.B. Hannay, Ed., Am. Chem. Soc. Monograph Series, Reinhold Publishing Co., New York, 1959; Proc. of the Conference on Semiconductor Compounds, J. Appl. Phys. 32, No. 10, 1961.

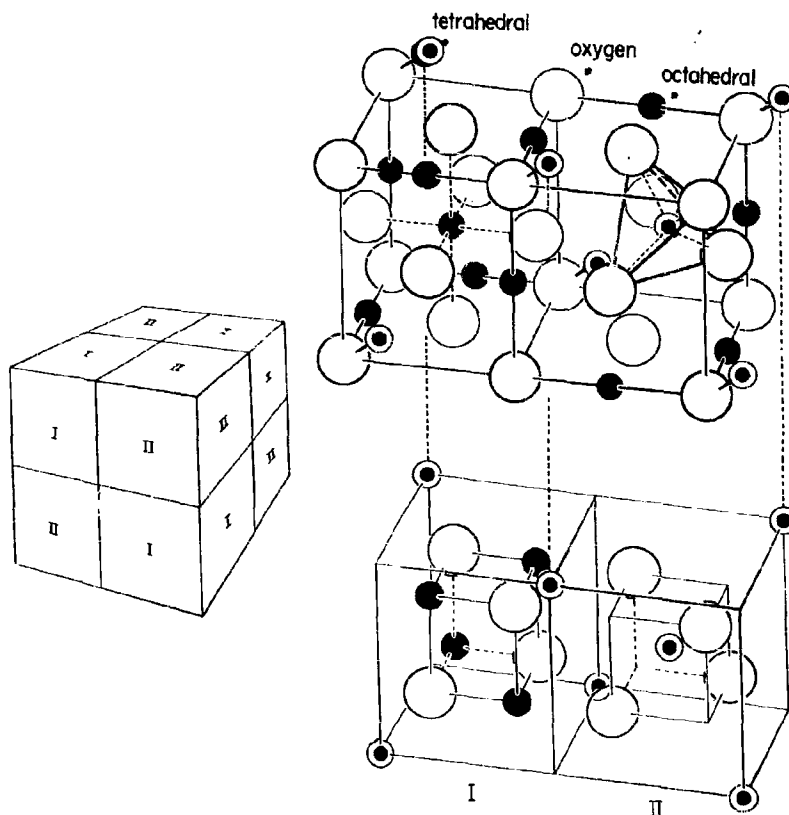


Fig. 24. Magnetite structure formed by cubic-close packed oxygen lattice and iron ions in interstitial sites.

The same is true for the ferrites,<sup>18)</sup> the semiconductors indispensable for magnetic high-frequency applications (memory devices, gyrators, etc.). Again the model of a close-packed array with interstitial sites (Fig. 22) helps to explain basic properties. Magnetite, the prototype ferrite ( $\text{Fe}_3\text{O}_4$ ) is formed - in ionic description - by a cubic close-packed  $\text{O}^{2-}$  sublattice; one quarter of its interstitial tetrahedral sites is occupied by  $\text{Fe}^{3+}$ , one half of its octahedral sites by  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  cations in a 1:1 ratio. The cations in this inverse spinel structure (Fig. 24) are so placed that the electrostatic repulsion is minimized. Since  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations in equal numbers occupy equivalent

18) Cf., e.g., J. Smit and H. P. J. Wijn, "Ferrites," John Wiley and Sons, New York, 1959.

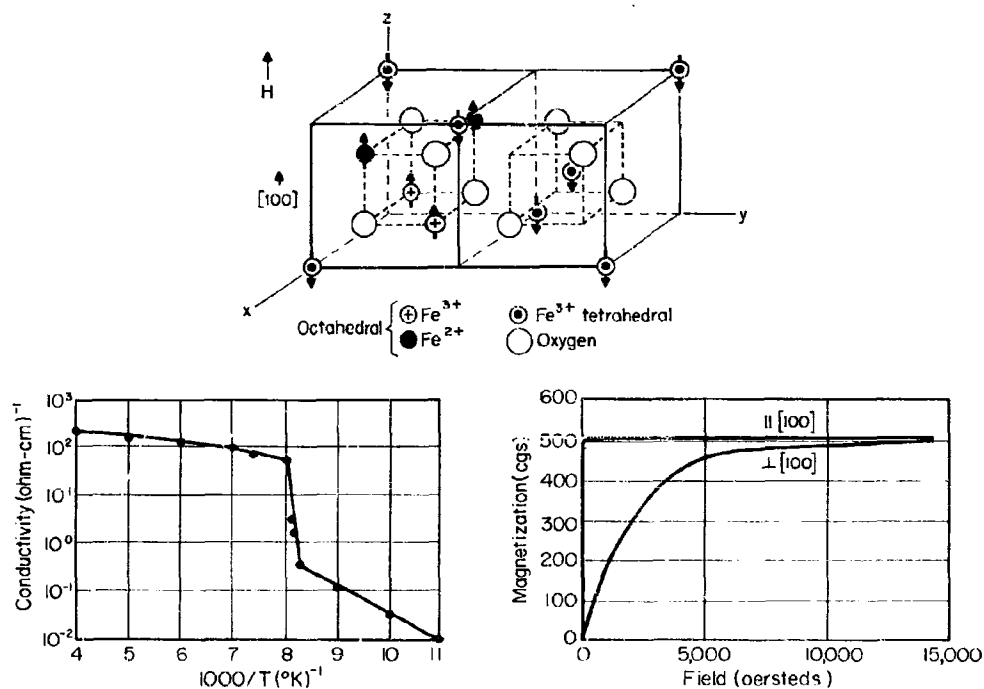


Fig. 25. Freezing-in of order in magnetite.

octahedral interstices, easy electron exchange between them makes magnetite too conductive for most purposes. The material can be transformed into an insulator by cation substitution blocking this electron transfer.

The unpaired electrons in the cations of the transition elements are the carriers of the magnetic moments in the ferrites. Electron exchange between  $\text{Fe}^{2+}$  (4 Bohr magnetons) and  $\text{Fe}^{3+}$  (5 Bohr magnetons) varies the magnetic arrangement at the same time. This coupling between electric and magnetic properties becomes clearly visible in magnetite by freezing-in an ordered sequence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  below  $-155^{\circ}\text{C}$ . The conductivity drops by several orders of magnitude, and if the magnetic spins are ordered by application of an external field while cooling through the transition, a magnetic axis is frozen-

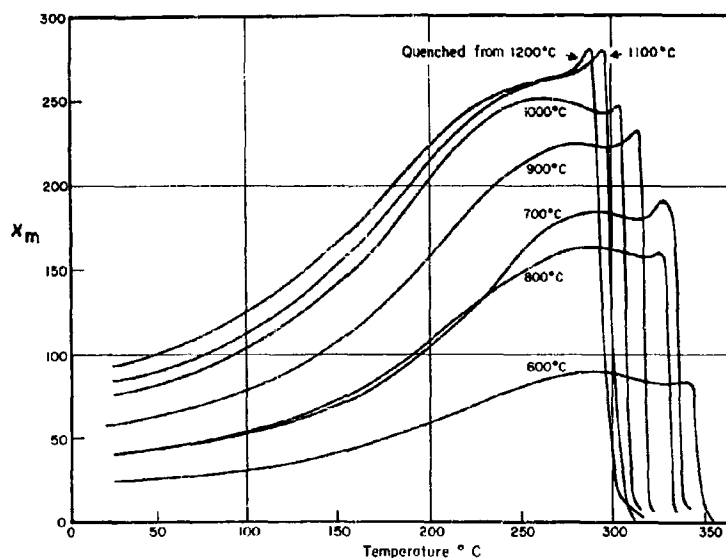


Fig. 26.  
Freezing-in of disorder  
in magnesium ferrite.

in, altering the hysteresis loop completely<sup>2,19)</sup> (Fig. 25). Vice versa, since in the ferrites only a fraction of the interstitial sites is occupied, high temperature extends the spread of cations to less favorable positions. In consequence, by quenching-in such disorder, the magnetic properties can be greatly affected (Fig. 26).

These examples must suffice. They show that the connection between structure and properties can be of obvious directness and, in other situations, buried in prehistory effects which challenge the tenacity of a psychoanalyst for their elucidation. The principal reasons for complications are the same as in living systems: A macroscopic phenomenon may be produced by a variety of molecular causes; furthermore, the phenomenon may not be related to the ideal structure of a material but to the faults built into such structure.

Science in previous times believed that "nature loves simplicity" and that man in his incredible complexity presents a "mighty effort contrary to nature." Dictatorships enslaving man could thus be justified as a return to

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19) B. A. Calhoun, Phys. Rev. 94, 1577 (1954).

nature's order. Today, this excuse of tyrants has vanished. Every day we learn with increasing insight that nature is incredibly complex and man one incident in its organization. At the outset we raised the question: What shall we most reasonably do with our natural resources? Molecular designing allows to realize Jule Verne's phantasies. The answer is therefore not any longer what we can do, but what we want to do. Molecular science and molecular engineering must operate as allies of social science and political statesmanship in imaginative planning for the most beneficial transformation of the world's resources.

#### Acknowledgements

The author is greatly indebted to his co-workers, Mr. C. W. Nelson and Mr. J. J. Mara, for help in preparing the figures.